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⑭積層化ポリオレフインフイルム

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明 細 書

1. 発明の名称
積層化ポリオレフインフイルム

2. 特許請求の範囲

(1) フイラーを10～40重量％含有する延伸ポリオレフインフイルム1と、このフイルム1の少なくとも片面に積層された表面光沢度30以下の延伸ポリオレフインフイルム2とからなる積層化ポリオレフインフイルム。

3. 発明の詳細な説明

この発明は、積層化ポリオレフインフイルムに関する。

従来、ポリオレフインにフイラーを含有せしめた組成物を延伸することにより、内部および表面にボイドを形成して白色、不透明化し、併せて表面を紙状光沢とするフイルムの製法が知られている。

しかし、このように内部及び表面にボイドを形成した延伸フイルムは、フイラーとボイドの存在のため、その後の加工時の摩擦、例えば印刷、印字および丸下抜取り等の作業で、紙状光沢を有する表層部分が剥離してくる欠点があつた。また、粘着テープ基体として使用する場合に、被着体が凹凸面あるいは弾性のある球面や曲面であると、剛がある（ヤング率が大きい）ために、カール等で被着体から剥離してくるなどの欠点もあつた。

この発明の目的は、上記欠点に鑑み、紙状で表層部分が剥離することなく、かつ凹凸面や曲面、ゴム質のように弾性のある球形面からなる被着体から剥離することのない、しかも水濡れ現象が防止され、且つ温度や湿度の変化にも安定な積層化ポリオレフインフイルムを提供することにある。

上記目的を達成するために、この発明は、つぎの構成を有する。すなわち、フイラーを10～40重量％含有する延伸ポリオレフインフイルム1と、このフイルム1の少なくとも片面に積層された表面光沢度30以下の延伸ポリオレフインフイルム2とからなる積層化ポリオレフインフイルムである。

この発明におけるフイラーを含む延伸ポリオレフインフイルム1とは、延伸によりフイラー周辺

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Particulars of KOKAI (Laid-Open) Specification

Patent KOKAI (Laid-Open) No. 59-49971

Laid-Open Date: March 22, 1984

Patent Application No. 57-159884

Application Date: September 14, 1982

Inventors: Satoshi Nagura and two others

Applicant: TORAY INDUSTRIES, INC.

Title of the Invention: Imitation Paper Polyolefin Film

Specification

1. Title of the Invention: Imitation Paper Polyolefin Film

2. Claim:

(1) An imitation paper polyolefin film, which comprises an oriented polyolefin film 1 containing 10 - 40 wt.% of a filler and an oriented polyolefin film 2 having a surface glossiness of 30 or less and further laminated on at least one side of said film 1.

3. Detailed Description of the Invention:

The present invention relates to an imitation paper polyolefin film.

Conventionally, methods for orienting resins comprising polyolefins containing fillers have been

known. The methods can produce films which are whitened and opaqued with voids formed within and on the surface, having a paper-like gloss on the surface.

These oriented films with the voids formed within and on the surface have been found to have certain drawbacks. Of the films, the surface portions having the paper-like gloss are inclined to be separated because of wear incidental to subsequent work, for example wear due to printing and typing or optical reading. The fillers and voids present in the films are responsible for this. If the films are adhered laminates, their great strength (with a high Young's modulus of elasticity) causes the surface portions to be separated from the adherends, if these adherends have uneven surfaces or flexible distorted surfaces or curved surfaces.

Accordingly, an object of the present invention is to find a solution to these drawbacks and provide an imitation paper polyolefin film having a surface portion which is not worn-off due to wear, is not separated from an adherend having an uneven surface, a curved surface or a distorted surface as flexible as rubber products, capable of preventing damage due to water spillage and having stability to changes in temperature and moisture.

In order to accomplish said object, the present invention provides an imitation paper polyolefin film, which comprises an oriented polyolefin film 1 containing 10 - 40 wt.% of a filler and an oriented polyolefin film 2 having a surface glossiness of 30 or less and further laminated on at least one side of said film 1.

According to the present invention, the oriented polyolefin films 1 containing the fillers are caused to form voids on the periphery of the fillers by the orientation. They have a low apparent specific gravity, retaining a mechanical strength and stability of measurements and developing flexible, white and opaque layers. Ordinarily, the films 1 are biaxially oriented. It is necessary that the films 1 should contain at least 50 wt.% of polypropylene resins as the resin component. Polypropylene resins may as well contain ethylene-propylene (random or block) copolymer resins or polyethylene resins. Preferably, however, the films 1 comprises polypropylene resins singly. As the filler, inorganic particles are used singly or with two or more in mixture, including calcium carbonate, magnesium carbonate, magnesium oxide, alumina, aluminum silicate, kaolin, kaolinite, talc, diatomaceous earth, dolomite, titanium oxide and zeolite, etc. Of these, mixtures containing calcium carbonate as the main

component are preferably used. The fillers are contained in an amount of 10 wt.% - 40 wt.%, preferably 15 wt.% - 35 wt.%. If the content of the fillers is less than 10 wt.%, white and opaque films cannot be obtained. On the other hand, if said content is more than 40 wt.%, resultant films are fragile since they are incapable of retaining the mechanical strength required. These possibilities are both undesirable. The oriented polyolefin films 1 containing these fillers may also contain various additives except for the fillers described as above, for example a thermostabilizer, anticxidant, weathering agent, antistatic agent and nucleating agent, etc.

Next, the oriented polyolefin films 2 have the characteristic of paper-like gloss, i.e. surface glossiness of 30 or less. Their surface layers are good in adhesion with ink and toner, etc. for printing and typing, unlikely to be separated on account of wear due to printing or typing work or optical reading of typed surfaces. The films 2 are at least uniaxially, preferably biaxially oriented. The films 2 comprise the resin components singly or in their mixture, including polypropylene resins, ethylene-propylene (random or block) copolymer resins, polyethylene resins, polybutadiene resins, poly-1-butene resins and ethylene-propylene-diene terpolymer resins.

Preferably, the films 2 comprise ethylene-propylene copolymer resins. These film layers may be added with various additives except for the fillers described as above.

An oriented polyolefin film 1 containing a filler and an oriented polyolefin film 2 can be incorporated into a composite oriented film of 2 layers ((1) / (2)) or 3 layers ((2) / (1) / (2)). It is preferable that the composite oriented film obtained as above has a thickness ratio (1) / (2) (in the case where the film 2 is disposed on either side of the film 1, the ratio is calculated in terms of the total thickness of three layers) of 4 or more (preferably 6 or more) between both the films 1 and 2; an apparent specific gravity of 0.80 or less; a Young's modulus of elasticity of 300 kg/mm^2 or less (preferably, 200 kg/mm^2); and light transmittance of 20 % or less.

The oriented polyolefin film 2 has a surface glossiness of 30 or less, preferably 20 or less as the surface characteristics. If it is intended for use as a film in printing or typing, the oriented polyolefin film 2 has a wet tensile strength of preferably 45 dyne/cm or more, preferably 50 dyne/cm or more on the surface to be printed or typed. The wet tensile strength of 45 dyne/cm or more can be obtained on the desired surface of said film 2 by subjecting the

surface to a corona discharge treatment in an atmosphere containing at least 5 % carbon dioxide. The surface planned for adhering works (the surface not to be printed, nor typed) can undergo ordinary corona discharge treatment.

As used herein, the technical terms have the following meanings: the apparent specific gravity can be obtained by determining a 10cm × 10cm piece of a test sample with a micrometer at first, obtaining the volume of the sample from the resultant thickness and area and multiplying this volume by the weight of the film; the Young's modulus of elasticity can be obtained by applying a tension to the sample lengthwise and widthwise at a stress rate of 20 mm/min., determining the characteristics of strength and extension and providing the gradient of a portion wherein the strength is proportionate to extensibility in the initial period of stretching; and light transmittance can be obtained in accordance with JIS-K6714, the surface glossiness in accordance with JIS-Z8741(2) and the wet tensile strength in accordance with JIS-J6768 respectively.

A composite oriented film of 2 or 3 layers as described above is provided with an adhesive layer by applying an adhesive agent comprising acrylic resin such as acrylate or copolymer thereof to a surface not

to be printed nor typed. The so processed surface is dried and laminated with release paper, for example glassine paper which has been treated with resin such as silicone. The adhesive agents to be used herein are not necessarily limited, but water-resistant resins of a solvent type acrylic resin are preferably used.

Said composite oriented film is provided with a printed & typed layer by printing pictures, patterns and letters, etc. on a surface of the oriented polyolefin film 2 by the use of an offset printing technique, gravure printing technique, seal printing technique and screen printing technique, etc. Along with printing or as an alternative to it, letters, signs and bar codes can be typed on the same surface of the film 2 by the use of impact printer or non-impact printer such as electrostatic transfer printer or ink jet printer. Prior to the printing and typing, an additional layer having improved permeability or adhesiveness of ink may also be provided on the film 2. In this case, it is necessary that the surface should not be worn off or separated due to wear which would occur when said surface is printed, typed and processed or used but should have a paper-like gloss. These characteristics will be provided preferably by a method for applying a 1-5 μ thick thin film comprising a filler made of inorganic particles and a resin

component, for example polyester resins or polyurethane resins, etc. The surface of the oriented polyolefin film 2 is good in the adhesion with this thin film layer, and it is quite unlikely that the thin film layer will be separated on account of wear and so on.

This adhered laminate as printed and typed above can be overlaminated with a transparent, tough, oriented plastic thin film by the medium of an adhesive agent, in order to protect the printed and typed portions of the laminate from severe wear, etc. of outside origins. As this protective thin film, a plastic film having a surface glossiness of 30 or less and light transmittance of 80 % or higher is suitably used. Examples of said plastic film include a composite film comprising a biaxially oriented polypropylene and an (biaxially or uniaxially) oriented ethylene-propylene block copolymer and so on.

The method for manufacturing a paper imitating polyolefin film of the present invention will be described below, with reference to an example.

(1) Manufacturing a composite oriented polyolefin film

A polyolefin (for example, polypropylene) resin containing a filler made of inorganic particles and a polyolefin resin (for example, an ethylene-propylene copolymer) are respectively placed on different extruders. Then, both the resins are

extruded respectively from different mandrels as 2 or 3 layers and made into the form of a sheet. Furthermore, this sheet is biaxially oriented lengthwise and widthwise sequentially, followed by the relaxation, heat treatment and surface treatment. In this way, a composite oriented polyolefin film of 2 layer ((1) / (2)) or 3 layer ((2) / (1) / (2)) laminate comprising a filler-containing oriented polyolefin film 1 and an oriented polyolefin film 2 is completed. Alternatively, this composite oriented polyolefin film can be manufactured by extruding a polyolefin resin containing a filler molding, orienting lengthwise, thereafter laminating a polyolefin resin which is melt-extruded by using a different extruder and mandrel on the surface of the filler-containing polyolefin resin, orienting thus laminated composite film widthwise, followed by relaxation, heat treatment and surface treatment.

(2) Conversion into tack paper

Of the composite oriented polyolefin film obtained in (1) above, the filler-containing oriented polyolefin film layer 1 (in case of a 2 layer structure) or the oriented polyolefin film layer 2 (in case of a 3 layer structure) is applied with an adhesive agent and laminated with release paper, to provide tack paper.

(3) Printing work and conversion into a form

Tack paper obtained in (2) above, in the shape of a roll, is printed by the use of the gravure printing technique, the seal printing technique, the offset printing technique, the screen printing technique and so on. So processed tack paper is finished with die-punching and tailings disposal.

Tack paper obtained in (2) above can undergo the offset printing technique and the screen printing technique, etc. in a flat sheet. Furthermore, tack paper obtained in (2) above is printed in the shape of a roll and processed into a form by punching holes, providing perforated lines and die-punching, etc. to complete paper intended for use as the form.

(4) Typing work

Paper intended for use as the form is set on a printer of a terminal processor and typed with carbon-containing oily ink and toner by the use of impact printer or non-impact printer of ink jet formula and electrophotographic formula. In this process, it is possible to type optically readable information, for example letter codes, mark codes and bar codes, etc.

(5) Overlaminating a protective layer

In the process of converting tack paper into a form as in (3) above, it is arranged that paper does not go through the steps of die-punching and tailings

disposal. Then, this paper intended for use as the form is typed as in (4) above, and thereafter, the typed surface thereof is overlaminated with a transparent, oriented plastic thin film by the medium of an adhesive agent.

(6) Applying a layer of high ink permeability

A layer of high ink permeability is applied on the surface of the oriented polyolefin film having the surface wet tensile strength of 45 dyne/cm or more, with respect to the composite oriented polyolefin film obtained in (1) above. Then, the layer of high ink permeability is dried, printed and converted into paper intended for use as the form as in (3) above and typed as in (4) above. This layer of high ink permeability is obtained by applying and drying polyester resin or polyurethane resin containing a filler made of inorganic particles in a thickness of 1-5 μ.

Fig. 1 - Fig. 4 are typical diagrams respectively showing the structure of the imitation paper polyolefin film of the present invention and that of products made therefrom. Accordingly, Fig. 1 shows an imitation paper polyolefin film (composite oriented polyolefin film) comprising a filler-containing oriented polyolefin film 1 and an oriented polyolefin film 2 which is laminated on one side of the film 1.

Fig. 2 shows a laminate which is obtained by providing the direct printing and typing 5 on the surface of the film 2 with respect to the imitation paper polyolefin film of Fig. 1.

Fig. 3 is a sectional view of a laminate which is obtained by providing the printing and typing 5 on the surface of the film 2 by the medium of a high ink permeability layer 6, with respect to the imitation paper polyolefin film of Fig. 1.

Fig. 4 shows a laminate which is obtained by providing the direct printing and typing 5 on the surface of the film 2 in the same way as in (2) above and laminating a protective film layer 8 on top of them by the medium of an adhesive agent layer 7. All the laminates shown in Fig. 2 - Fig. 4 are laminated with release paper on their back by the medium of an adhesive agent layer 3.

As described above, the imitation paper polyolefin film of the present invention comprises an oriented polyolefin film containing 10-40wt% of a filler and an oriented polyolefin film having a surface glossiness of 30 or less and further laminated at least on a side of the other film. Accordingly, paper-like adhered plastic laminates made therefrom are stable against breakages due to water spillage and changes of temperature and humidity. Their printed or typed

portions are not worn-off due to wear and so on, nor are they separated from adherends having an uneven surface, curved surface or distorted surface as flexible as a rubber product, with appropriate follow-up adhesiveness. Therefore, the imitation paper polyolefin film of the present invention can find a wide application as the display labels of, for example frozen foods, refrigerated foods and wet foods; and as the display labels of POS (point of sales) related products in the distribution & inventory management systems and those of blood bags in the fields relating to the blood gathering or transfusion. Particularly in the processes for using these display labels, the surface layers are not wiped off even if they are wiped with cloths in a wet state at the time of cooling or heating incidental to refrigerating, freezing or thawing. Furthermore, the surface layers are not worn-off due to wear that would occur as the films are contacted by light pens at the time of optical reading. Furthermore, if the adherends deform by shrinking or swelling as in the case of blood bags, the display labels are not separated from them, nor even from the curved surface of test tubes. Therefore, the imitation paper polyolefin film of the present invention will be suitably used in fields wherein these characteristics are required.

The example of the present invention will be described below, along with comparative examples.

(Example)

(1) Polypropylene resin having a MI (Melt Index defined by ASTM- D1238) of 1.0, resin containing 20 wt.% of calcium carbonate having a particle size of 1.7 μ and ethylene-propylene block copolymer resin comprising 20 wt.% of an ethylene component having a MI of 6.0. were co-extruded from a mandrel for 2 layers and molded. The resultant product was biaxially oriented lengthwise (3.5 times) and widthwise (9 times) sequentially and then thermoset. Thereafter, one side of the product (a surface of the ethylene-propylene block copolymer layer) was subjected to the corona discharge treatment in an atmosphere containing carbon dioxide. The other side of the product also was treated with the corona discharge in the air. In this way, a composite polyolefin film of 90 μ was obtained.

This composite biaxially oriented ethylene polyolefin film was found to comprise 8 μ of an ethylene-propylene block copolymer layer and 82 μ of a polypropylene layer containing a filler. Of them, the ethylene-propylene block copolymer layer was found to have a surface wet tensile strength of 52 dyne/cm and a

surface glossiness of 15. The filler-containing polypropylene film layer was found to have a wet tensile strength of 36 dyne/cm. Furthermore, this composite biaxially oriented polyolefin film was found to have the properties wherein the specific gravity was 0.60, the Young's modulus of elasticity was 103 kg/mm^2 lengthwise and 180 kg/mm^2 widthwise and light transmittance was 15 %.

(2) With respect to the composite biaxially oriented polyolefin film obtained in (1) above, the filler-containing polypropylene film layer was applied with an acrylate adhesive agent, dried and laminated with glassine paper which had previously been treated for silicone mold release.

(3) The adhered laminate obtained in (2) above was cut in a width of 15 inches and converted into paper intended for use as a form by printing in color by the use of offset printing technique, punching holes at a side, providing perforated lines and die-punching. The adhered laminate which was converted into paper intended for use as a form as above was typed with a bar code of blood type information on the die-punched white surface by the use of a toner containing carbon in a wet type electrostatic transfer printer of System 8500 (a printer manufactured by TORAY INDUSTRIES, INC.). The toner was fixed at 110 °C × sec.

(4) The adhered laminate typed with the bar code as above was separated from release paper, put on a blood bag made of non-rigid PVC and immersed in water in a state of being folded up small for 24 hours. Thereafter, water was wiped off from the adhered laminate ten times, and then, the portions typed with the bar code were read out by a bar code scanner.

The blood bag was folded up, immersed in water, taken out therefrom and wiped off with cloths as it was in a wet state. But it was found that the adhered laminate which had been put on the blood bag was not broken or separated, remaining adhered by following up the deformation of the adherend. It also was found that the bar code of blood type information could be read out as it was inputted by the use of an optical scanner and that the printed and typed surface was free of any breakages or changes in measurements.

(Comparative Example 1)

Paper-like adhered plastic laminate of coating type 60 μ of transparent (light transmittance of 92 %), biaxially oriented polypropylene film (a film treated with the corona discharge in the air, and having a surface wet tensile strength of 36 dyne/cm) was coated on the surface with approximately 10 μ of

polyester resin containing 20 wt.% of calcium carbonate by using a reverse-roll coater. The mixture was dried, to complete a paper-like plastic film of coating type.

The so obtained film was found to have the properties of a specific gravity of 0.86, a Young's modulus of elasticity of 200 kg/mm^2 lengthwise and 350 kg/mm^2 widthwise and light transmittance of 23 %.

An adhered laminate was prepared from the paper-like plastic film of coating type by repeating the procedure as described in (2) of the Example.

(Comparative Example 2)

Paper-like adhered plastic laminate having surface voids.

Polypropylene resin containing 20 wt.% of calcium carbonate as described in Example was melted, extruded and molded. The resultant product was biaxially oriented lengthwise (3.5 times) and widthwise (9 times) sequentially, thermoset and subjected to corona discharge treatment in air, to obtain a paper-like plastic film of 90 μ having voids formed within and on the surface. The resultant film was found to have a specific gravity of 0.58, a Young's modulus of elasticity of 93 kg/mm^2 lengthwise and 150 kg/mm^2 widthwise and light transmittance of 14.5 %. An

adhered laminate was prepared from this paper-like plastic film having voids on the surface by repeating the procedure as described in (2) of the Example.

On the adhered laminate of the present invention as obtained in the Example, the adhered laminate of coating type plastic as obtained in Comparative Example 1 and the adhered laminate of paper-like plastic having voids on the surface, the offset printing was provided by using ink of "UV cure type flash dry S" brand from TOYO INK MFG. CO., LTD. The offset printing was finished with the UV irradiation and with typing of bar code by the use of a wet type electrostatic transfer printer. Thereafter, every adhered laminate was relieved of release paper, stuck to the non-rigid PVC adherend and immersed in water in a state of being folded up for 24 hours. After it was taken out of water, the so stuck laminate was wiped with a piece of cloth to remove water and then underwent a rub test in a state of being stuck Thereafter, a Scotch tape test was conducted to determine how much the laminate is separated from the adherend and how closely ink is adhered to the printed portions. A readout test also was conducted to determine if the bar codes typed on the surface can be read by the contact of a light pen in association with a bar code scanner.

Table 1 shows the results of these tests.

Table 1

	Rub test	Scotch tape text (adhesiveness of printing ink, surface strength)	Optical readout test (resistance to wear due to the contact of light pen, reading out)
Example: paper-like adhered plastic laminate(present invention)	○	○	○
Comparative Example 1: paper-like adhered plastic laminate of coating type	×	×	×
Comparative Example 2: paper-like adhered plastic laminate with voids on the surface	×	×	×

(Test methods)

Rub test:

An adhered laminate layer is stuck to a non-rigid PVC adherend and both of them are rubbed with both hands 50 times, to determine how far the adhered laminate is separated from the adherend and how much the adhered laminate and the printed portions thereof are broken.

Scotch tape test:

A cellotape, Nichiban & Co.'s brand of Scotch tape, in a size of 18 mm wide ×50 mm long is stuck to a printed portion and is caused to separate by 180 degrees, to determine how much printing ink is separated and how much the surface layer is broken.

Optical readout test:

A portion typed with bar code is scanned 50 times while it is worn away by the contact of a light pen (Laser Scanning Head) running at an angle of 45 degrees to the portion, in association with a Model 2243 scanner from Monark Marking System. Resistance of typed surface layer to wear and accuracy of readout (the result is rated as x, if even one failure occurs in a bout of scanning 50 times) are determined.

The meanings of Table 1 will be described in detail below.

The adhered laminate of the present invention was also stuck to a flexible adherend made of non-rigid PVC, and they underwent a rub test. As a result, it was found that the adhered laminate of the present invention was excellent as it was not separated from but remained adhered to the adherend by following the deformation of the latter. Furthermore, the printed portion and the surface portion were found not to be shaken off. In contrast, it was found that the adhered laminate of coating type was partially separated from the adherend and that the printed portion and the coated surface layer were shaken off partially, along with sprinkling of powder. Furthermore, the adhered laminate having the voids on the surface was found not to be separated from the adherend, but the printed portion and the surface void layer were partially broken or shaken off, along with sprinkling of powder. These shortcomings cannot be tolerated.

The Scotch tape test resulted in an outcome that follows: with respect to the adhered laminate of the present invention, the printed portion and the surface layer base material were found to be free of any of separation, breakage and shakeoff. In contrast, it was found that the printed portion and the surface

layer were partially broken and shaken off from the adhered laminates of either coating type or having the voids on the surface, accompanied by sprinkling of powder, and that their optical readout was impossible. These shortcomings cannot be tolerated.

In the test of optical readout of typed bar codes, it was found that the adhered laminate of the present invention was not in the least adversely affected on the printed portion and the surface base material by wear due to the contact of light pens, permitting the appropriate optical readout.

In contrast, with respect to the adhered laminate of coating type, the coated layer was found to be broken or shaken off because of wear due to the contact of the light pens, along with sprinkling of powder, and the optical readout of the typed bar codes was impossible. In the adhered laminate having the voids on the surface, the surface layer was found to be broken because of wear due to the contact of the light pens and unreceptive to the optical readout.

As described above, the adhered laminate of the present invention is more flexible than the other adhered laminates either of coating type or having the voids on the surface as obtained in the Comparative Examples and further excellent in adhesiveness of ink and high in the surface strength.

4. Brief Description of the Drawings:

Fig. 1 is a typical sectional view of a paper imitation polyolefin film of the present invention. Fig. 2-Fig. 4 are typical sectional views of products made therefrom.

1 ... an oriented polyolefin film containing a filler, 2 ... an oriented polyolefin film having a surface glossiness of 30 or less.

Fig. 1

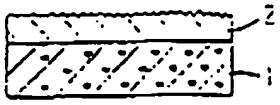

Fig. 2

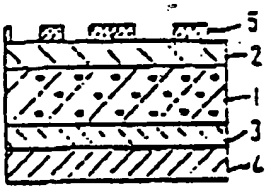

Fig. 3

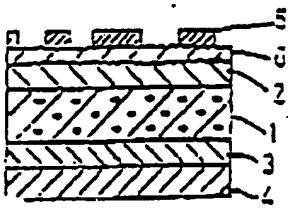

Fig. 4